

"Express Mail" Mailing Label Number EL581514885US

Date of Deposit: JULY 24, 2000

I hereby certify that this paper or fee is being deposited with the United States Postal Service "Express Mail" Post Office to Addressee" service under 37 C.F.R. 1.10 on the date indicated above and is addressed to:

Assistant Commissioner for Patents Washington D.C. 20591

By: Ben TRELLA

*Insert*  
*AI*

## METHOD OF RADIATION TREATMENT FOR FLUOROPOLYMER MATERIALS

### Background of the Invention

The present invention relates to a method and apparatus for irradiating fluoropolymer materials. It finds particular application in conjunction with the irradiation of polytetrafluoroethylene (PTFE), fluorinated ethylene propylene (FEP), and chlorotrifluoroethylene (CTFE) to degrade their mechanical properties. It is to be appreciated, however, that the present application is also applicable to the radiation treatment of other polymeric materials to alter chemical resistance, electrical properties, thermal stability, surface properties, and other characteristics.

Finally, milled PTFE is used as a common additive to inks and to lubricants. However, PTFE is an extremely tough material with very strong bonds. It is extremely difficult to mill into a fine powder.

In order to facilitate the milling process, radiation has been used to break chemical bonds in the PTFE polymer chains. In one technique, Teflon material was placed in open containers in a cobalt 60 ( $^{60}\text{Co}$ ) vault. Gamma rays from the cobalt 60 irradiated the PTFE for a duration which weakened the bonds sufficiently, typically on the order of several hours.

In another technique, PTFE material, in granules, sintered shavings, or other thin, small pieces was placed in an open tray. The tray was passed slowly through an accelerated electron beam irradiating the PTFE material. The product was raked or stirred and passed through the electron beam again.

These techniques have several drawbacks. First, a significant quantity of hydrogen fluoride (HF) gas is released into the atmosphere. Hydrogen fluoride is highly corrosive and toxic to workers in the environment. Other 5 toxic and corrosive gases, including fluorene, are also released. Further, treatment of PTFE in open containers releases PTFE dust into the environment which settles on walkways and other surfaces. PTFE is an extremely slippery lubricant creating fall and other injury hazards 10 to workers. Moreover, the PTFE dust in the environment can be breathed by the workers. The present invention contemplates a new and improved fluoropolymer material irradiations apparatus and method which overcomes the above referenced problems and others.

15

#### Summary of the Invention

In accordance with one aspect of the present invention, a method of irradiating fluoropolymer materials is provided. Oxygen and oxygen containing gases are removed from an irradiation chamber. The chamber is 20 irradiated with penetrating, ionizing radiation. The fluoropolymer material is passed through the ionizing radiation in the oxygen and oxygen containing gas depleted environment of the irradiation chamber.

In accordance with more limited aspects of the 25 present invention, the gases removed from the irradiation chamber include air and water vapor.

In accordance with a yet more limited aspect of the present invention, the irradiation chamber is evacuated.

30 In accordance with another more limited aspect of the present invention, the penetrating radiation is accelerated electrons.

In accordance with another more limited aspect 35 of the present invention, the fluoropolymer material is in particulate form and the particles are rotated by magnetic or electrical fields.

In accordance with a yet more specific aspect of the present invention, irradiation of the fluoropolymer particles by the electron beam charges the dielectric fluoropolymer particles creating rotational forces.

5           In accordance with another aspect of the present invention, an apparatus is provided for irradiating fluoropolymer materials. A radiation source generates a beam of radiation which passes through an irradiation chamber. A vacuum pump draws down oxygen, oxygen  
10          containing gases, water vapor, and other gases from the irradiation chamber. A source of fluoropolymer materials supplies a fluoropolymer material to the irradiation chamber.

15          One advantage of the present invention is that it reduces the generation of toxic and corrosive gases.

Another advantage of the present invention is that it reduces and substantially eliminates the distribution of dust and toxic substances into the environment.

20          Another advantage of the present invention resides in improved worker safety.

Still further advantages and benefits of the present invention will become apparent to those of ordinary skill in the art upon reading and understanding 25 the following detailed description of the preferred embodiments.

#### Brief Description of the Drawings

The invention may take form in various components and arrangements of components, and in various 30 steps and arrangements of steps. The drawings are only for purposes of illustrating preferred embodiments and are not be construed as limiting the invention.

FIGURE 1 is a diagrammatic illustration of a fluoropolymer material irradiation system in accordance 35 with the present invention;

FIGURE 2 is an alternate embodiment of a fluoropolymer irradiation system; and,

5 FIGURE 3 is a graphic illustration of fluorine gas evolution rate versus radiation dose in air at atmospheric pressure and at vacuums of  $10^{-1}$  to  $10^{-5}$  Torr.

Detailed Description of the Preferred Embodiments

A particle accelerator 10 accelerates electrons, preferably in the 1-15 MeV range. A beam of the electrons are conveyed to a scan horn 12 which fans the electron beam out over an elongated region. An irradiation treatment chamber 14 is mounted immediately contiguous to the scan horn to receive the electron beam. Preferably, the irradiation chamber has a height and width which are commensurate with height and width of the fanned electron beam from the scan horn. To minimize electron beam losses, the scan horn and irradiation chamber are separated only by a thin foil layer, preferably aluminum foil.

20 The irradiation chamber 14 is interconnected with a vacuum pump 20 which removes air from the irradiation chamber. Preferably, the vacuum pump draws a vacuum on the order of  $10^{-1}$  to  $10^{-3}$  Torr. The irradiation chamber is also connected with a source 22 of fluoropolymer material. Preferably, the fluoropolymer 25 material is in particulate, shaving, or flake form. The fluoropolymer material moves through the evacuated treatment chamber 14 at a controlled rate. Preferably, the material has a dwell time in the irradiation chamber of about one minute. On impact, the charged electrons not 30 only break chemical bonds but also impact an electrical charge to the dielectric fluoropolymer particles.

After the fluoropolymer material has passed through the irradiation chamber, it passes through a cooler 24 which removes heat accumulated during the 35 irradiation process. Cooling reduces the amount of gases generated. That is, at higher temperatures, particularly

100-4369-2A2D

above about 110°C, the rate at which toxic gases are generated increases. The cooled and irradiated material passes to a separator 26, such as a cyclone separator, where it is deposited. The separator includes a vacuum sealed valve, such as a rotary pocket valve 28 through which accumulated irradiated fluoropolymer material is passed for receipt and appropriate packaging.

More specifically to the preferred embodiment, a valve 30 in one position connects an outlet port of the 10 vacuum pump 20 through a filter and toxic gas recovery system 32 to the atmosphere while the system is drawn down to the preferred pressure level. After the system is drawn down to the preferred pressure level, the valve 30 connects the pump 20 to a pneumatic return path 34 15 extending to the fluoropolymer material source 22 to make a closed loop pneumatic path. The valve 30 can be operated intermittently to maintain the vacuum in the pneumatic path. An entraining mechanism 36 entrains the material into the low level of recirculated gas. The 20 entraining mechanism may include, for example, a rotary pocketed vacuum valve 38 for passing the fluoropolymer material at a metered rate into the vacuum side of the system. A nozzle or venturi type arrangement 40 assists in entraining the material particles into the moving gas.

In order to agitate or stir the material 25 particles as they pass through the reaction chamber, a series of magnets 42 of alternating polarity line the walls of the irradiation chamber. As each charged fluoropolymer particle moves into an opposite polarity 30 region, the electromagnetic forces flip its orientation. The magnets are preferably strong magnets such as samarium cobalt or barium permanent magnets. Alternately, electrical coils can be placed on sides of the irradiation chamber to turn the electrostatically charged particles by 35 electric field changes. Agitation can also be provided mechanically by baffles in the chamber 14.

Various alternate techniques are also contemplated for moving the material through the treatment chamber 14. For example, the material can be moved through the chamber with a mechanical conveyor, such as a belt or auger. As another example, the particles can fall by gravity. As yet another example, the material can be formed into ribbons or tubes that are pulled through the evacuated chamber. Numerous other conveying techniques will be apparent to those of ordinary skill in the art.

With reference to FIGURE 2, in a batch-processing embodiment, fluoropolymer material in particulate or flake form is placed in a relatively flat, wide container 50 which is sealed to the environment. The container is connected to a vacuum pump 52 which draws a vacuum therein, again preferably on the order of  $10^{-1}$  Torr or less. After evacuation, the container 50 is preferably disconnected from the vacuum pump. The evacuated container is placed on a flat belt or other conveyer system 54 for carrying the conveyer below a ceiling mounted scan horn 56. The container is passed through the beam one or more times until a selected dose is achieved. A pulsed particle accelerator 58 again accelerates particles which are focused and aimed by the scan horn through the material in the container 50. Electrical windings or magnets 60 of alternating polarity are disposed adjacent the scan horn for stirring or agitating particles in the container 50.

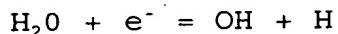
Optionally, a cooling system 62 is placed below the belt to cool the material that has been heated by the electron beam. Preferably, the electron beam has an energy in the 1-5 MeV range. The container is moved back and forth until the Teflon particles have received about 30-150 Mrad of radiation, more preferably 100-120 Mrad. This can typically be achieved with a total cumulative radiation time of about one minute.

The fluoropolymer materials have long fluorocarbon chains which are broken by the oxidizing

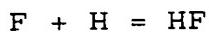
effect of the electrons into smaller chains and chain segments including some short  $C_2F_4$  chain segments. In the ionizing environment of the irradiation chamber, some of the short chains degrade into free or reactable carbon and fluorine molecules.



Analogously, water vapor in environmental air is also ionized:



10          The free hydrogen and fluorine react to form hydrogen fluoride:



The remaining carbon and hydroxide radicals react to form carbon dioxide and hydrogen gas. Analogously, other  $C_2F_4$  radicals react directly with oxygen from the air and free hydrogen from ionized water vapor to form  $-CF_2COOOH + HF$ . By removing the oxygen and water vapor by drawing a significant vacuum, the amount of oxygen and water vapor available to engage in the reactions which form hydrogen fluoride are greatly reduced, greatly reducing the generation of hydrogen fluoride.

Even if a small amount of hydrogen fluoride and fluorine gases are still generated, such gases continue to be circulated through the system. A rise in the pressure 25 due to these gases does not increase the generation of hydrogen fluoride or fluorine, so long as oxygen and water vapor are not introduced into the system. Alternately, rather than maintaining a vacuum, the system can be evacuated of oxygen and water vapor and replaced with an 30 inert gas or other gas which does not adversely interact with fluoropolymer materials to form hydrogen fluoride or other toxic gases.

Optionally, other forms of radiation can be utilized, including gamma rays and higher energy x-rays. 35 However, being lower in energy than the electron beam, gamma and x-radiation will require longer irradiation times to achieve the same degree of treatment.

The electron beam is preferably pulsed. Pulsing the electron beam provides alternate irradiation and cooling periods for the treated particles. Typically, the electron beam is scanned back and forth across the scan horn. The scanning, again provides intermittent irradiation or alternating irradiation and cooling periods. Typical e-beam radiation settings include 1.0-5.0 MeV electron beam with a pulsed beam current of 1-5 kA and a pulse duration of 10-500 n sec.

Although a vacuum of  $10^{-1}$  to  $10^{-3}$  Torr is preferred, higher vacuums achieve a further reduced rate of hydrogen fluoride and fluorine gas generation.

With reference to FIGURE 3, curve 70 illustrates the rate of fluorine gas generation in milligrams per MGy of radiation dose in air at atmosphere pressure and at various vacuum levels. Curve 72 illustrates the generation rate of hydrogen fluoride versus dose for  $10^{-1}$  Torr vacuum levels; curve 74 for  $10^{-2}$  Torr; curve 76 for  $10^{-4}$  Torr; and curve 78 for  $10^{-5}$  Torr. It will be noted that while  $10^{-1}$  torr produces satisfactory results, results at  $10^{-2}$  torr are again significantly improved with a gas generation at  $10^{-4}$  torr or lower greatly improved.

The invention has been described with reference to the preferred embodiments. Obviously, modifications and alterations will occur to others upon reading and understanding the preceding detailed description. It is intended that the invention be construed as including all such modifications and alterations insofar as they come within the scope of the appended claims or the equivalents thereof.